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OFFICE OF CONTRACT ADMINISTRATION
SPONSORED PROJECT INITIATION

no action 60 days ahl

Date: 3/10/77

Project Title: "Development of High Dielectric Constant Slip-Cast Material for Use in Fabricating Large Dielectric Domes".

Project No: A-1965

Project Director: Mr. J. N. Harris

Sponsor: SPERRY, Microwave Electronics, Clearwater, Fla. 33518

Agreement Period: From 3/1/77 Until 4/15/77

Type Agreement: P.O. No. 38023-HL

Amount: $4,649.00

Reports Required: Final Report at end of contract period.

Sponsor Contact Person (s):

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Defense Priority Rating: under DMS Reg. 1

Assigned to: Applied Sciences (School/Laboratory)

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SPONSORED PROJECT TERMINATION

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Date: August 5, 1977

Project Title: Development of High Dielectric Constant Slip-Cast Material for Use in Fabricating Large Dielectric Domes

Project No: A-1965

Project Director: J. N. Harris

Sponsor: Sperry Microwave Incorporated

Effective Termination Date: 7/31/77

Clearance of Accounting Charges: 7/31/77

Grant/Contract Closeout Actions Remaining:

- x Final Invoice and Closing Documents
- _ Final Fiscal Report
- _ Final Report of Inventions
- _ Govt. Property Inventory & Related Certificate
- _ Classified Material Certificate
- _ Other _____

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A-1965

ENGINEERING EXPERIMENT STATION
GEORGIA INSTITUTE OF TECHNOLOGY • ATLANTA, GEORGIA 30332

July 26, 1977

Sperry Microwave Incorporated
Box 4648
Clearwater, Florida 33518

Attention: Dr. Felice D'Angelo, MS 21

Subject: Final Report, "Development of High Dielectric Constant Slip-Cast Material for Use in Fabricating Large Dielectric Domes," Sperry P. O. No. 38023-HL, Georgia Tech Project A-1965.

Gentlemen:

A. Introduction

The Sperry Microwave Corporation has a requirement for a hemispherical dielectric dome nominally 36 inches in diameter, with a dielectric constant of 25 and a loss tangent of less than 0.005. Dielectric properties must be homogeneous and wall thickness must taper from about ½ to 2½ inches over various portions of the hemispherical wall. In addition, a coating is required of a lower dielectric constant material.

The ceramic slip casting process is adaptable to this requirement, large shapes can be fabricated with homogeneous properties, and coatings of different dielectric constant can be easily and permanently applied.

In order to increase the dielectric constant of the composite ceramic material two things must be done to the slip casting system. These are:

(1) Add a high dielectric constant material to act as a dispersed phase in the basic matrix material. The dispersed phase must retain its integrity and not melt or diffuse into the matrix.

(2) The particle size distribution of the high dielectric constant material must "match" the distribution of the matrix material. That is, it must not disrupt the particle packing characteristics of the matrix material. It is desirable that the modified slip system produce a casting with a porosity that is no greater than the porosity of the basic system.

The effects of adding a high dielectric constant dispersed phase to an existing slip-cast ceramic material can be determined with "off-the-shelf" high dielectric constant materials, however, problems will exist in obtaining the

lowest possible porosity. The problem of maximizing density requires special order high dielectric constant materials with lead times of many months. These materials would then be ball milled with the basic slip casting material to produce a well dispersed broad distribution of all materials. This would require a relatively high man-power effort of 6 months or more and should only be undertaken after investigating the effects of readily available high dielectric constant powders on the dielectric properties of composite mixtures. The current program used readily available powders that were not of the proper size distribution to minimize porosity, with the knowledge that measured dielectric constant would be lower than with an optimized particle system. The objectives were:

(1) To prepare slip-cast specimens and measure dielectric properties.

(2) To determine how much material could be added to the basic system with out disrupting casting properties.

(3) To determine effects of additives on firing characteristics.

(4) To determine homogeneity of dielectric properties on relatively large specimens.

(5) To predict dielectric constants of high density materials with additives of proper particle size distribution to maximize particle packing.

B. Background

The Georgia Institute of Technology has over 20 years experience in fabricating ceramic radomes by the slip casting process. A large number of both thin and thick wall shapes have been fabricated from slip-cast fused silica. Shapes up to 31 inches in diameter and up to 52 inches in height have been slip-cast and sintered at Georgia Tech and even larger shapes have been cast, then transported to local manufacturing facilities for sintering. In the course of this work the fused silica slips have been modified with various additives to increase thermal conductivity, improve emittance, and improve rain erosion capabilities. Fabricated structures have been monolithic (single density), layered structures of greatly differing densities, and modified silica coatings applied in thin layers to the basic fused silica structure.

The slip casting process is a relatively simple fabrication technique. A wide particle size distribution of ceramic particles is suspended in a liquid and is called a slip. This suspension is then poured into a plaster mold where the liquid is removed by capillary action. Wall thickness of hollow shapes is controlled by time of casting. When the proper thickness is attained the

remaining slip is removed from the mold. A second method of controlling wall thickness is to place an impervious model inside the plaster mold which defines the desired shape. Different layers of material can be built up by placing a slip in the plaster mold, casting a layer to the desired thickness, removing the slip and immediately replacing with the next slip. This can be continued for as many layers as desired.

In the case of fused silica slip it is typically an 82.5 percent solids suspension in water. Particle size varies from 50 micrometers to submicrometer size with the mean, on a mass basis, typically 7 to 8 micrometers. This material when sintered at 1250° C produces a part with 8 to 10 percent total porosity (90 percent dense). Dielectric constant at x-band and room temperature is 3.4 with a loss tangent of 0.001. Similar work has been conducted with alumina slips but to a much lesser extent.

These slips can be modified by adding other particulate materials, but care must be taken that the added materials do not affect packing density. Usually the addition of fine particulate material results in a lower casting density and a more porous structure. The dispersed phase must have very large particles or a distribution closely matching the distribution of the matrix. A complete exposition on particle packing is beyong the scope of this program, however, references (1-5) give detailed information on particle packing in particulate systems.

Kingery (6) has investigated mechanical mixtures of dielectrics and compared equations for estimating the dielectric constant of composite mechanical (not chemically combined) mixtures of ceramic particulate materials. He cites several equations but finds the log mixing rule

$$\log \varepsilon_r = V_1 \log \varepsilon_1 + V_2 \log \varepsilon_2 \qquad (1)$$

where V = volume fraction of each component

ε = dielectric constant of each component.

To give a good prediction particularly when the dispersed phase has a much higher dielectric constant than the matrix material, Kingery (6) suggests that the log mixing rule is not particularly applicable in estimating the effects of porosity where the pores act as the low dielectric constant material dispersed in the high dielectric constant matrix. He suggests in this case that a better estimate may be obtained using the equation:

$$\varepsilon_r = V_1 \varepsilon_1 + V_2 \varepsilon_2 \qquad (2)$$

However, experience at Georgia Tech with actual measurement of the dielectric constant of fused silica foams with up to 80 percent porosity has shown that the best estimates are obtained using the log mixing rule. When porosity alone is being considered, Equation (1) can be rewritten as:

$$\varepsilon_r = \varepsilon_o^{1-P} \qquad (3)$$

where P equals the volume fraction pores.

The slip casting systems available for modification are fused silica and alumina. Typical high dielectric constant materials which could be added as a dispersed phase are titania, barium titanate and strontium titanate. Properties of these materials are shown in Table I.

TABLE I

DENSITY AND DIELECTRIC CONSTANT FOR MATRIX MATERIALS AND HIGH DIELECTRIC CONSTANT ADDITIVES

Material	Density (gm/cm^3)	Dielectric Constant
Fused Silica (SiO_2)	2.22	3.85
Alumina (Al_2O_3)	3.97	9
Titania (TiO_2)	4.17	90
Strontium Titanate ($SrO\ TiO_2$)	---	250
Barium Titanate ($BaO \cdot TiO_2$)	5.85	1100

Figures 1 through 3 show the expected effects of adding up to 50 volume percent titania, strontium titanate and barium titanate to fused silica and alumina

matrices. The data in these figures are based on the log mixing rule, (Equation (1)). Figure 4 shows the estimated effects of porosity on a dielectric constant of 50 using both Equations (2) and (3). Based on these data one would anticipate that it would be easier to achieve the desired dielectric constant of 25 by modifying an alumina slip. However, the alumina slips have a narrow range of stability with respect to viscosity and pH and are susceptible to rapid change and instability with the addition of foreign materials. Therefore, it is anticipated that the best possibility of success lies in the modification of fused silica slips.

C. Experimental Procedure

Dielectric grades of barium and strontium titanates were ordered from Transelco Incorporated, Penn Yan, New York. While waiting receipt of these materials work was initiated with an on-hand pigment grade of titania which had been sintered to coalesce it into larger particles. This material was ball milled and screened through a 325 mesh screen to give a particle distribution from 44 micrometers to submicrometer size. Unfortunately, there was only enough of this material to prepare two compositions with fused silica slip. The first composition contained 31.5 volume percent titania and the second 49.9 volume percent. Both of these compositions were cast into 2 inch diameter discs approximately 3/8 inch in thickness, dried and sintered at 1035° C. The first composition, containing 31.5 volume percent titania, fired out to a smooth disc with a bulk volume of 2.16 gm/cm^3 (estimated 23.8 percent porosity). The second composition shrank excessively, cracked and was very porous and friable.

The barium and strontium titanates received from Transelco were very finely divided and had particle sizes of 2.0 and 1.8 micrometers respectively. Because of the large surface area involved modifications other than a direct addition to the slip had to be made to obtain mixtures fluid enough to be cast. These included the addition of coarse particles of silica and alumina. Even minute additions of strontium titanate formed gummy mixtures which could not be cast. The addition of dispersants did not lower the viscosity of these mixtures, therefore, attempts to use strontium titanate were discontinued.

Numerous compositions were prepared with the finely divided barium titanate and mixtures of fused silica and alumina. Some had excessive drying and/or firing shrinkage and cracked on drying or firing. Some would not sinter and others melted. Only those that slip-cast and fired with low shrinkage and no cracking were submitted for dielectric measurements. The most successful compositions were prepared with the components shown in Table II.

These discs plus the two discs made with 31.5 volume percent titania were shipped to Quartzite Processing Incorporated, to be machined into shorted

TABLE II

VOLUME COMPOSITION OF SAMPLES SUBJECTED TO DIELECTRIC TESTING

Sample No.	Barium Titanate	Fused Silica Slip	-200 Mesh Fused Silica Grain	-40 Mesh Alumina
1A	0.275	0.725		
2B	0.41		0.32	0.27
6A	0.40			0.60
6B	0.29	0.22		0.49
7B	0.13	0.87		

waveguide specimens for dielectric measurement at 9.375 GHz. The specimens were machined into rectangles 0.892 in. x 0.392 in. x thickness. The machined specimens were thoroughly dried then measured and weighed to calculate bulk density. Theoretical density was calculated using the volume fraction and specific gravities of all components. The bulk density and calculated theoretical density were used to estimate porosity. The expected dielectric constant was calculated based on the composite theoretical density using Equation (1) and corrected for porosity using Equation (3). At the time the specimens were machined a reasonable estimate of the porosity, and hence of the dielectric constant was not available. Therefore, the sample thickness was not adjusted for estimated dielectric constant. When the samples were measured using the shorted waveguide technique at 9.375 GHz three values were reported. Initial measurements were made on 22 April 1976. The samples were then machined to half their original thickness and again measured on 16 May using the shorted waveguide technique at 9.375 GHz. Attempts were then made to pick the correct value for dielectric constant. All of this data is reported in Table III.

The samples were then shipped to Dr. D'Angelo at Sperry Microwave for measurements at different frequencies. Dr. D'Angelo measured two samples containing

TABLE III

ESTIMATED AND MEASURED DIELECTRIC PROPERTIES OF SLIP-CAST SPECIMENS

Sample No.	Calc Sp.G. (gm/cm^3)	Meas Bulk Density (gm/cm^3)	Estimated Porosity (%)	Est Diel Constant (w/o pores)	Est Diel Constant (w/pores)	Measured Diel Constant (4/22)	Measured Diel Constant (5/16)	Measured Loss Tangent (4/22)	Measured Loss Tangent (5/16)
1A	3.22	1.78	0.45	18.2	4.9	4.41	4.4	0.007	0.01
						13.00	21.0	0.0008	0.003
						26		0.001	
2B	4.18	2.62	0.37	49.2	11.5	8.85	8.9	0.05	0.06
						19.30		0.05	
						34.00	34.0	0.05	0.06
6A	4.72	3.26	0.31	61.5	17.2	9.85	9.5	0.01	0.02
						21.85		0.01	
						38.00	38	0.014	0.02
6B	4.13	2.54	0.38	27.0	7.6	7.19	6.5	0.03	0.06
						15.76		0.02	
						28.00	27	0.02	0.03
7B	2.69	1.70	0.37	8.0	3.7	3.57	3.15	0.008	0.006
						22.60	19.75	0.001	
						39.00		0.001	0.0003
1T	2.83	2.16	0.24	10.4	5.9	7.65	7.87	0.002	0.01
						19.50		0.0009	
						37.00		0.006	
2T	2.83	2.17	0.23	10.4	6.1	7.87	7.7	0.005	0.006
						19.30		0.002	
						46.00		0.007	

barium titanate and found a considerable shift with frequency in both dielectric constant and loss tangent. These changes may be due to either the ferroelectric nature of barium titanate or melting of the components to form a glass.

In measuring other samples at various frequencies at Georgia Tech, the dielectric constant shift and high losses were not observed with the samples containing titania or the samples containing only barium titanate and silica. Unfortunately, since samples could not be fabricated with the available strontium titanate it was not possible to determine whether this material would cause high losses at high frequencies.

The remaining funds were used in attempts to make larger specimens for microwave measurements at Sperry Microwave. At the request of Dr. D'Angelo large flat discs were prepared in lieu of the hemispheres suggested in the proposal.

A number of 3¼ inch diameter specimens were prepared with barium titanate before the problem of high loss tangent was recognized. Several attempts were made to prepare dense specimens of the same size with titania, but due to the particle distribution available the samples prepared were too porous. None of the specimens were measured for dielectric properties due to exhaustion of available funds, however, these specimens are available for shipment to Sperry Microwave for further examination. Information on these 3¼ inch diameter specimens are shown in Tables IV and V.

TABLE IV

COMPOSITION OF BARIUM TITANATE-ALUMINA SPECIMENS

Specimen (no.)	$BaTiO_3$ (vol f)	Al_2O_3 -40 Mesh (vol f)	Al_2O_3 -100 Mesh (vol f)	Al_2O_3 -325 Mesh (vol f)	Estimated Porosity (%)	Estimated ε_r
1E	0.22		0.22	0.56	46	5.8
2E	0.18		0.26	0.56	49	4.8
3E	0.25	0.375		0.375	44	6.7
4E	0.40			0.60	43	10.5

TABLE V

COMPOSITION OF TITANIA-FUSED SILICA SPECIMENS

Specimen (no.)	TiO_2 (vol f)	SiO_2 (vol f)	Estimated Porosity (%)	Estimated ε_r
1F	0.404	0.596	45	4.2
2F	0.492	0.508	43	5.2

D. Discussion

An examination of Figure 1 shows that the maximum dielectric constant attainable by adding titania to fused silica slip while retaining the fused silica as the matrix (limit of 50 volume percent titania) is of the order of 18.5. It is unreasonable to expect that porosity can be decreased below about 10 percent, therefore, the highest dielectric constant possible with a dispersed titania phase in silica would be of the order of 13 to 14. Similarly, with alumina as the matrix, the maximum dielectric constant is of the order of 28.5 and with 10 percent porosity it is of the order of 20. Therefore, if the characteristics of the two basic slip systems, (1) fused silica, and (2) alumina are to be retained, higher dielectric constant additives to act as the dispersed phase are needed.

Two titanates were selected on the basis of dielectric constant alone. An examination of Figures 2 and 3 indicates that with silica, potential dielectric constants of 31 and 63 could be obtained with 50 volume percent of strontium and barium titanates respectively. With alumina potential dielelectric constants of 47 and 99 are possible with 50 volume percent of the same two titanates.

As anticipated desired densities could not be achieved due to the fine particle size of the titania and the titanates. The strontium titanate was so fine that compositions could not be prepared with this material. Castable compositions were prepared with fused silica slips containing 31.5 percent titania and 27.5 percent barium titanate by volume. In both cases porosity of the final sintered part was higher than desired because the fine particle additives did not allow

optimum packing of the material. The important point is that good solid castings were obtained with increases in dielectric constant appropriate to the amount of high dielectric constant material added and the degree of porosity of the sintered part. With the fused silica slips the high dielectric additive was well dispersed and did not separate (settle out of suspension during casting). Although only small parts were fabricated, it is believed that these slips could have been used to cast large, intricate shapes which would have had homogeneous dielectric properties throughout the shape.

Higher loadings of barium titanates were achieved by making "artificial" slips using larger grain sizes of fused silica (74 micrometers) and alumina (420 micrometers). These were not true slip suspensions, but were thick stiff mixtures which had to be vibrated into the molds for casting. These types of casting systems can also be used to form large intricate shapes, but are more difficult to work with than fluid slip casting systems.

Several attempts were made to add the titania and barium titanate powders to alumina slips, but these attempts were unsuccessful. Even very small additions of these powders caused the alumina slips to become too viscous to pour.

Good estimates of the measured dielectric constant were obtained using the log mixing rule and correcting for porosity for those compositions containing only fused silica slip and barium titanate. For those samples containing fused silica slip and titania the log mixing rule gave values slightly lower than those measured when correcting for porosity using the log mixing rule and values slightly higher than those measured when using Equation (2) as suggested by Kingery (6). The estimated dielectric constant was way off from actual measured values for specimems 2B and 6A. This may indicate a chemical combination of component materials rather than each component remaining as intermixed discrete particles. These two specimens and specimen 6B had a distinct yellowish color which is an indication of some chemical combining. All three specimens contain alumina (Al_2O_3). Two similar compositions containing 33 percent barium titanate, 43 percent silica and 24 percent alumina actually metled in the kiln at the sintering temperature of 1100^{o} C used for all the samples containing titanates. Another indication of glass formation is the high loss tangent measured for all three specimens. An examination of Table III shows reasonable loss tangents for all other specimens which contain only fused silica and barium titanate or titania.

Further measurements were made on samples 2B and 6A by Dr. D'Angelo. These measurements indicated a large shift in dielectric constant with frequency and high loss as had been indicated by measurement at Georgia Tech. It is obvious from these measurements that mixtures of barium titanate with alumina should not be considered further. The data obtained with fused silica and

barium titanate was satisfactory at room temperature and at the measured frequency of 9.375 GHz. It is not known whether there will be a shift in dielectric properties, due to changing frequency of temperature, with barium titanate additives to fused silica due to the ferroelectric nature of barium titanate. These compositions should be investigated further. Fused silica-titania compositions are not expected to be lossy or to show drastic shifts in dielectric constant with changing temperature and/or frequency. This leaves two potential approaches for achieving a material with the desired dielectric constant of 25 and loss tangent of 0.005.

(1) Continue the investigation of barium titanate or strontium titanate additions to fused silica slip. The titanate particle size must be optimized to minimize porosity in the modified fused silica hardware.

(2) Develop a titania slip casting material modified to lower the dielectric constant by adding a fused silica particulate material.

Prior to initiating a full scale developmental program on fused silica slips modified with titanates additional investigations should be made using compositions 1A and 7B. Hemispherical shapes should be cast and dielectric specimens cut from various parts. These should be used to measure dielectric constant at room temperature, elevated temperatures and several frequencies. This would determine the homogeneity of the material and its dielectric stability. If both homogeneity and stability are good then a larger program should be initiated to optimize particle packing by obtaining special order titanates with large particle diameter which could be blended with the fused silica slip by ball milling.

The second approach would require titania with a particle size greater than -325 mesh (44 micrometers) which could be ball milled to form a slip. This slip could be modified by the addition of fused silica to lower its dielectric constant. Figure 5 shows the expected dielectric constant for porous parts made with 70, 80 and 90 percent titania modified with fused silica. Such a program as this would require several months to obtain the proper particle size starting material and to develop a suitable slip. This second approach would be favored in that it gives a greater flexibility in obtaining the desired dielectric characteristics. Stability of the dielectric constant with frequency and temperature should be better and loss tangent lower than with the titanates.

E. Conclusions

1. High dielectric constant additives can be dispersed in fused silica slips thereby increasing the dielectric constant and retaining a low loss tangent.

2. Both titanium oxide and barium titanate were dispersed in fused silica giving an increased dielectric constant while retaining low loss tangent for measurements at 9.375 GHz and room temperature.

3. Modified fused silica slips with greater than 30 volume percent additive can be formulated and still retain excellent casting and firing characteristics.

4. Additions of coarse particle titania to fused silica slip allowed a larger percentage of additive and a lower final porosity than additions of fine particle titania.

5. Barium titanate mixed with aluminum oxide appears to combine chemically at sintering temperatures of 1100° C and produce compositions that show large shifts in dielectric constant with respect to frequency. These compositions also have large loss tangents.

F. Recommendations for Future Work

A short program should be initiated to measure the dielectric properties of the current fused silica modified with barium titanates with respect to temperature and frequency. If the desired stability is not achieved with these compositions they should be dropped and development of a titania slip casting material pursued. If these compositions do indicate they can meet stability requirements particularly with the barium titanate, then attempts should be made to obtain coarser barium titanate and optimize the particle distribution of this material in the already developed fused silica slip.

Respectfully submitted,

Joe N. Harris
Project Director

jw

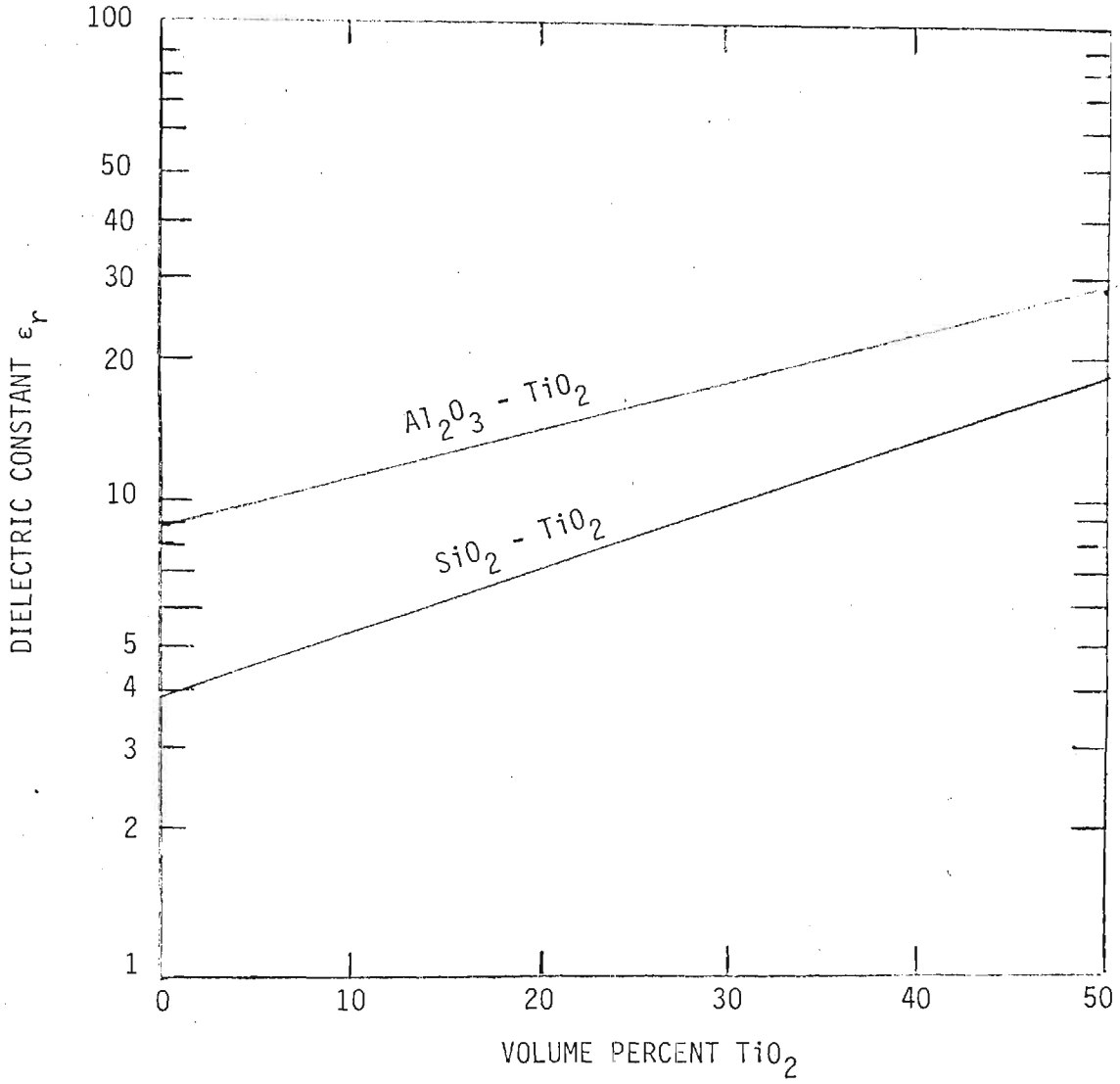

Figure 1. Dielectric Constant for Fused Silica and Aluminum Oxide Modified With Titanium Oxide.

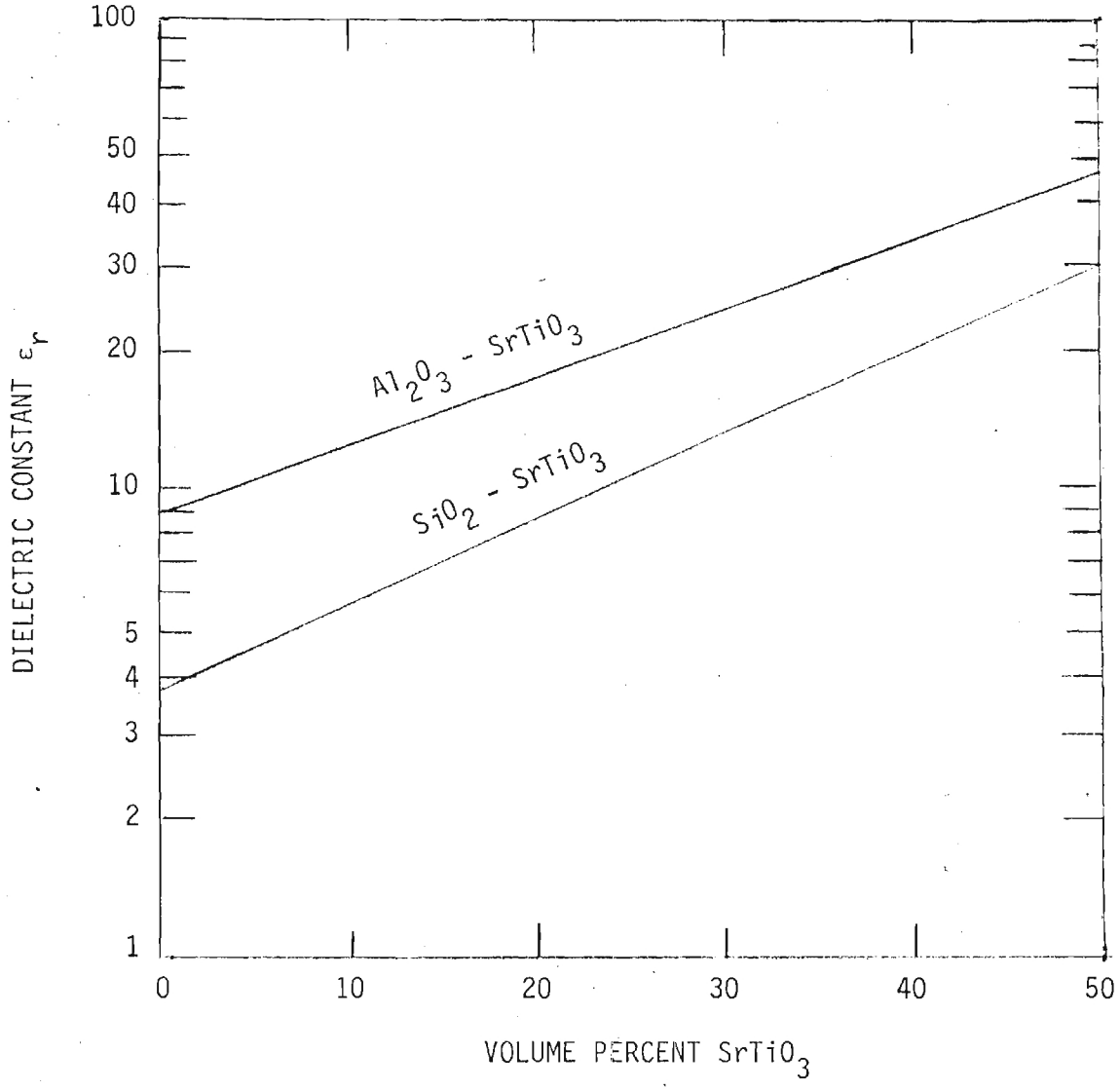

Figure 2. Dielectric Constant for Fused Silica and Aluminum Oxide Modified with Strontium Titanate.

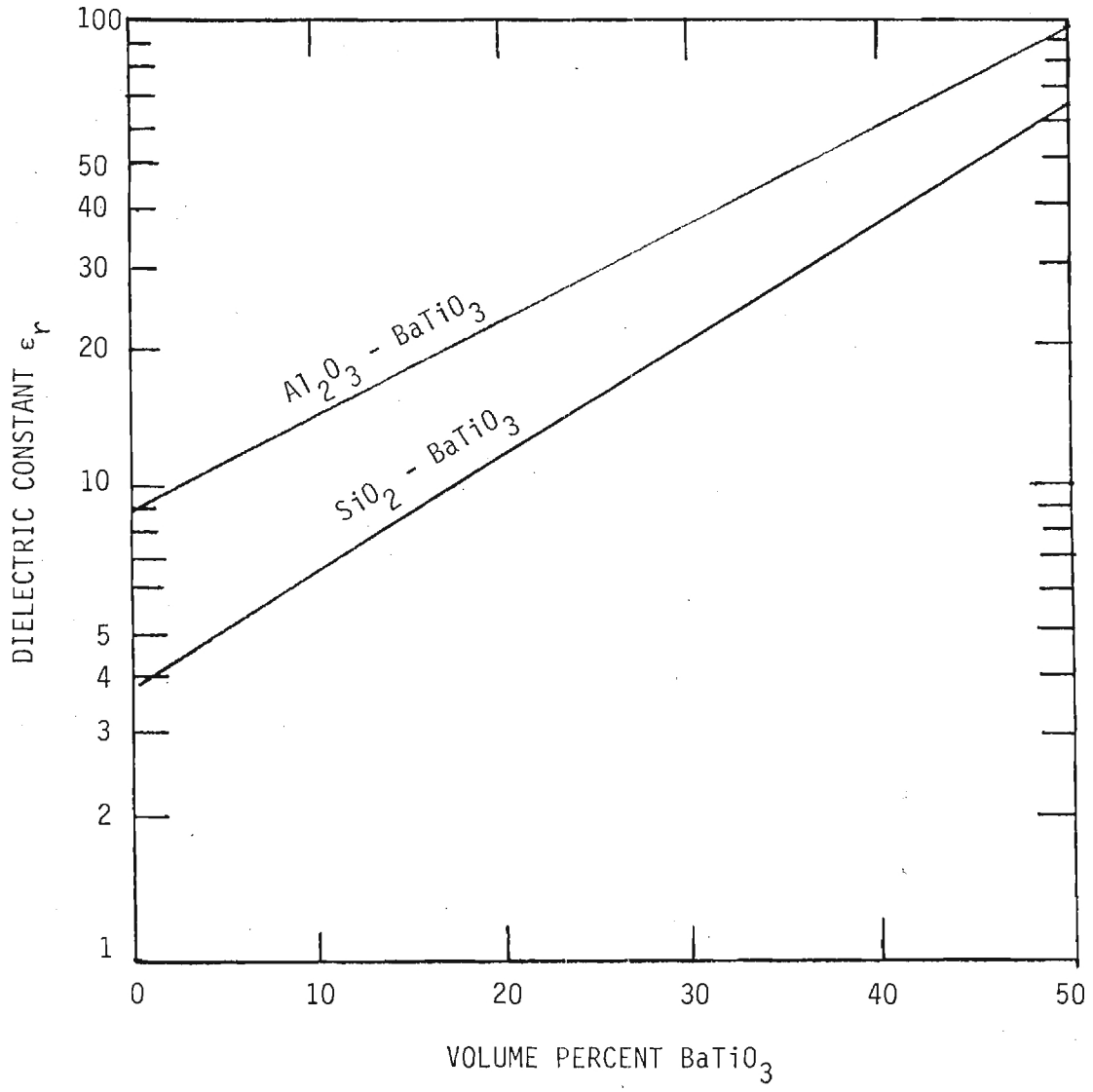

Figure 3. Dielectric Constant for Fused Silica and Aluminum Oxide Modified with Barium Titanate.

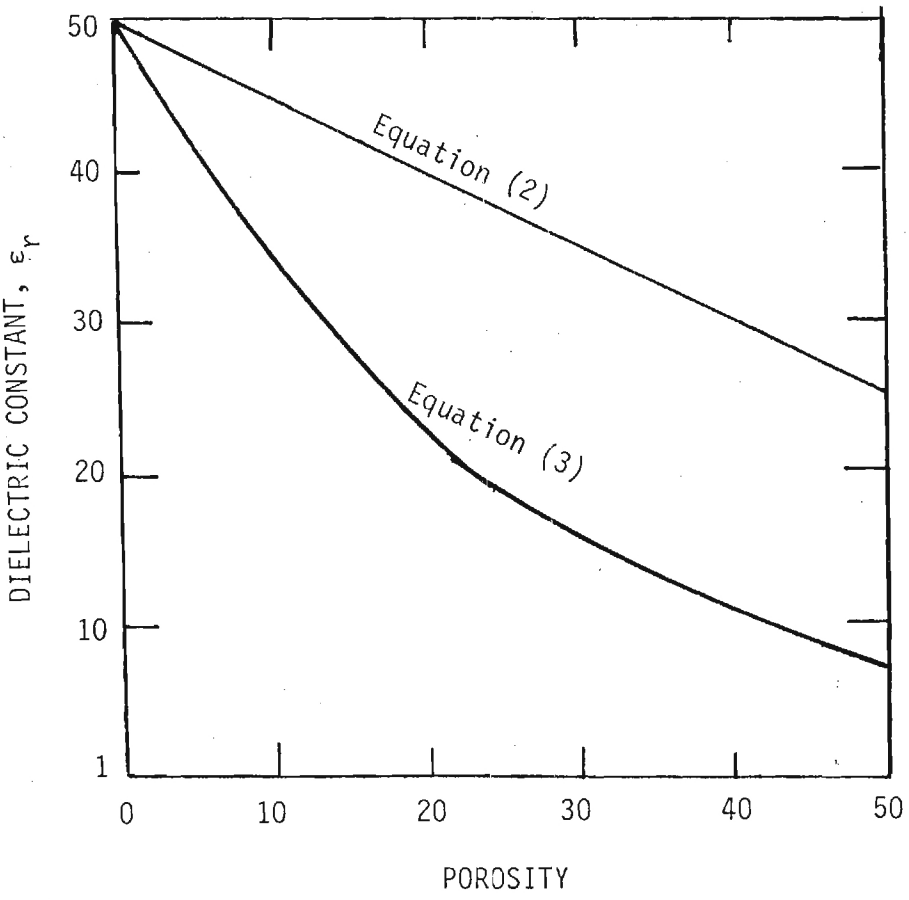

Figure 4. Estimated Effect of Porosity on Dielectric Constant Using Kingery's Equations.

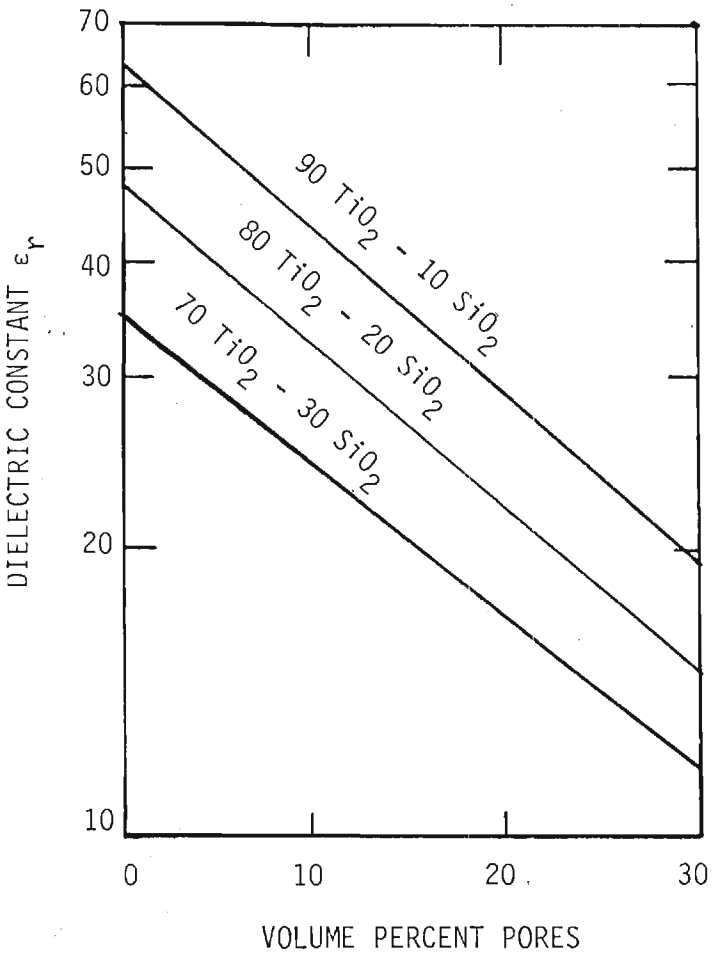

Figure 5. Estimated Dielectric Constant and Effect of Porosity on TiO_2 - SiO_2 Slip-Cast Parts.

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